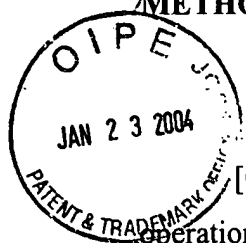


# METHODS AND COMPOSITIONS FOR THE DIVERSION OF AQUEOUS INJECTION FLUIDS IN INJECTION OPERATIONS

## BACKGROUND OF THE INVENTION



[0001] The present invention relates to compositions and methods useful in injection operations. More particularly, the present invention relates to fluids comprising water-soluble relative permeability modifiers and methods of using such fluids to divert aqueous fluids in injection operations.

[0002] Generally, in the recovery of hydrocarbons (*e.g.*, oil) from a subterranean formation, the energy required to force the hydrocarbons into producing wells may be supplied by the natural pressure drive existing in the formation or by mechanically lifting hydrocarbons from the subterranean formation through the wells bores of producing wells to the surface. But at the end of primary recovery operations, a substantial quantity of hydrocarbons may remain in the subterranean formation. Thus, secondary recovery methods, such as injection operations, may be used. For example, in injection operations the energy for producing the remaining hydrocarbons from the subterranean formation may be supplied by the injection of fluids into the formation under pressure through one or more injection wells penetrating the formation, whereby the injection fluids drive the hydrocarbons to one or more producing wells penetrating the formation. Suitable injection fluids include, among other things, water, steam, carbon dioxide, and natural gas. The sweep efficiency of injection operations, however, may vary greatly depending on a number of factors, such as variability in the permeability of the formation. In particular, where the subterranean formation contains high permeability zones, the injection fluids may flow through the areas of least resistance, *e.g.*, through the high permeability zones, thereby bypassing less permeable zones. While injection operations may provide the energy necessary to produce hydrocarbons from the high permeability zones, hydrocarbons contained within less permeable zones may not be driven to the one or more production wells penetrating the formation.

A variety of techniques have been attempted to improve the efficiency of injection operations. One such technique, known as "polymer flooding" comprises the addition of water-soluble polymers, such as polyacrylamide, to the injection fluid, *inter alia*, in order to achieve a higher viscosity injection fluid. A higher viscosity injection fluid may result in a better sweep efficiency of the injection fluid in the displacement of hydrocarbons through the formation

because the viscosified injection fluid may be less likely to by-pass the hydrocarbons, leaving them behind in the formation. One drawback to this technique is that despite the increased viscosity, the polymer flood may still flow through the high permeability zones, bypassing the oil contained within less permeable zones of the formation.

[0003] Another technique to increase the efficiency of injection operations has involved the injection of a sealant, such as polymer gels, into the subterranean formation so as to plug off the high permeability zones. Thus, the flow of the injection fluids may be diverted from the high permeability zones to less permeable zones. The use of these water-blocking techniques, however, may be problematic. For example, plugging off the high permeability zones may not be suitable unless the sealant can be injected solely into the offending high permeability zones therein. Furthermore, techniques geared toward injecting sealant designed to plug off the high permeability zones are limited because they may require expensive zonal isolation. Zonal isolation also may be inaccurate, which may lead to inadvertently plugging and/or damaging additional zones other than the high permeability zone.

## **SUMMARY OF THE INVENTION**

[0004] The present invention relates to compositions and methods useful in injection operations. More particularly, the present invention relates to fluids comprising water-soluble relative permeability modifiers and methods of using such fluids to divert aqueous fluids in injection operations.

[0005] An exemplary method of the present invention for performing an injection operation comprises: introducing a water-soluble relative permeability modifier comprising a hydrophobically modified water-soluble polymer into a subterranean formation; and injecting an aqueous injection fluid into the subterranean formation after introducing the water-soluble relative permeability modifier.

[0006] Another exemplary method of the present invention for performing an injection operation comprises: introducing a water-soluble relative permeability modifier comprising a hydrophilically modified water-soluble polymer into a subterranean formation; and injecting an aqueous injection fluid into the subterranean formation after introducing the water-soluble relative permeability modifier.

[0007] Another exemplary method of the present invention for performing an injection operation comprises: providing a water-soluble relative permeability modifier comprising a water-soluble polymer without hydrophobic or hydrophilic modification; introducing the water-soluble relative permeability modifier into a subterranean formation; and injecting an aqueous injection fluid into the subterranean formation after introducing the water-soluble relative permeability modifier.

[0008] An exemplary embodiment of a permeability-modifying treatment fluid of the present invention comprises a water-soluble relative permeability modifier comprising a hydrophobically modified water-soluble polymer.

[0009] Another exemplary embodiment of a permeability-modifying treatment fluid of the present invention comprises a water-soluble relative permeability modifier comprising a hydrophilically modified water-soluble polymer.

[0010] Another exemplary embodiment of a permeability-modifying treatment fluid of the present invention comprises a water-soluble polymer without hydrophilic or hydrophobic modification.

[0011] The features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the exemplary embodiments which follows.

## DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0012] The present invention relates to compositions and methods useful in injection operations. More particularly, the present invention relates to fluids comprising water-soluble relative permeability modifiers and methods of using such fluids to divert aqueous fluids in injection operations. As used herein, “relative permeability modifier” refers to a compound that is capable of reducing the permeability of a subterranean formation to aqueous-based fluids without substantially changing its permeability to hydrocarbons.

[0013] In certain embodiments of the present invention, the water-soluble relative permeability modifiers comprise a hydrophobically modified water-soluble polymer. As used herein, “hydrophobically modified” refers to the incorporation into the hydrophilic polymer structure of hydrophobic groups, wherein the alkyl chain length is from about 4 to about 22 carbons. In another embodiment of the present invention, the water-soluble relative permeability modifiers comprise a hydrophilically modified water-soluble polymer. As used herein, “hydrophilically modified” refers to the incorporation into the hydrophilic polymer structure of hydrophilic groups. In yet another embodiment of the present invention, the water-soluble relative permeability modifiers comprise a water-soluble polymer without hydrophobic or hydrophilic modification.

[0014] The hydrophobically modified water-soluble polymers used in the present invention typically have a molecular weight in the range of from about 100,000 to about 10,000,000. In exemplary embodiments, the hydrophobically modified water-soluble polymers may comprise a polymer backbone comprising polar heteroatoms. Generally, the polar heteroatoms present within a polymer backbone of the hydrophobically modified water-soluble polymer include, but are not limited to, oxygen, nitrogen, sulfur, or phosphorous.

[0015] In certain embodiments of the present invention, the hydrophobically modified water-soluble polymers may be a reaction product of a hydrophilic polymer and a hydrophobic compound that are capable of reacting with each other. Such hydrophobically modified water-soluble polymers may be prereacted before they are placed into the subterranean formation or they may be formed by appropriate reaction *in situ*.

[0016] The hydrophilic polymers suitable for forming the hydrophobically modified water-soluble polymers used in the present invention should be capable of reacting with hydrophobic compounds. Suitable hydrophilic polymers include, homo-, co-, or terpolymers

such as, but not limited to, polyvinylamines, poly(vinylamines/vinyl alcohols), and alkyl acrylate polymers in general. Additional examples of alkyl acrylate polymers include, but are not limited to, polydimethylaminoethyl methacrylate, polydimethylaminopropyl methacrylamide, poly(acrylamide/dimethylaminoethyl methacrylate), poly(methacrylic acid/dimethylaminoethyl methacrylate), poly(2-acrylamido-2-methyl propane sulfonic acid/dimethylaminoethyl methacrylate), poly(acrylamide/dimethylaminopropyl methacrylamide), poly (acrylic acid/dimethylaminopropyl methacrylamide), and poly(methacrylic acid/dimethylaminopropyl methacrylamide). In certain embodiments, the hydrophilic polymers contain reactive amino groups in the polymer backbone or as pendant groups, which are capable of reacting with hydrophobic compounds. In an exemplary embodiment, the hydrophilic polymers comprise dialkyl amino pendant groups. In an exemplary embodiment, the hydrophilic polymers comprise a dimethyl amino pendant group and at least one monomer comprising dimethylaminoethyl methacrylate or dimethylaminopropyl methacrylamide.

[0017] In certain exemplary embodiments, the hydrophilic polymers may comprise a polymer backbone comprising polar heteroatoms, wherein the polar heteroatoms present within a polymer backbone of the hydrophilic polymers include, but are not limited to, oxygen, nitrogen, sulfur, or phosphorous. Suitable hydrophilic polymers comprising polar heteroatoms within a polymer backbone include homo-, co-, or terpolymers such as, but not limited to, celluloses, chitosans, polyamides, polyetheramines, polyethyleneimines, polyhydroxyetheramines, polylysines, polysulfones, and starches. In an exemplary embodiment, the starch is a cationic starch. A suitable cationic starch may be formed by reacting a starch, such as corn, maize, waxy maize, potato, tapioca, and the like, with the reaction product of epichlorohydrin and trialkylamine.

[0018] The hydrophobic compounds that are capable of reacting with the hydrophilic polymers of the present invention include, but are not limited to, alkyl halides, sulfonates, sulfates, and organic acid derivatives. Examples of suitable organic acid derivatives include, but are not limited to, octenyl succinic acid; dodecenyl succinic acid; and anhydrides, esters, and amides of octenyl succinic acid or dodecenyl succinic acid. In certain exemplary embodiments, the hydrophobic compounds may have an alkyl chain length of from about 4 to about 22 carbons. For example, where the hydrophobic compound is an alkyl halide, the reaction between the hydrophobic compound and hydrophilic polymer may result in the quaternization of at least

some of the hydrophilic polymer amino groups with an alkyl halide, wherein the alkyl chain length is from about 4 to about 22 carbons.

[0019] In other exemplary embodiments, the hydrophobically modified water-soluble polymers used in the present invention may be prepared from the polymerization reaction of at least one hydrophilic monomer and at least one hydrophobically modified hydrophilic monomer. Examples of suitable methods of their preparation are described in U.S. Patent No. 6,476,169, the relevant disclosure of which is incorporated herein by reference.

[0020] A variety of hydrophilic monomers may be used to form the hydrophobically modified water-soluble polymers useful in the present invention. Examples of suitable hydrophilic monomers include, but are not limited to homo-, co-, and terpolymers of acrylamide, 2-acrylamido-2-methyl propane sulfonic acid, N,N-dimethylacrylamide, vinyl pyrrolidone, dimethylaminoethyl methacrylate, acrylic acid, dimethylaminopropylmethacrylamide, vinyl amine, vinyl acetate, trimethylammoniummethyl methacrylate chloride, methacrylamide, hydroxyethyl acrylate, vinyl sulfonic acid, vinyl phosphonic acid, methacrylic acid, vinyl caprolactam, N-vinylformamide, N,N-diallylacetamide, dimethyldiallyl ammonium halide, itaconic acid, styrene sulfonic acid, methacrylamidoethyltrimethyl ammonium halide, quaternary salt derivatives of acrylamide, and quaternary salt derivatives of acrylic acid.

[0021] A variety of hydrophobically modified hydrophilic monomers also may be used to form the hydrophobically modified water-soluble polymers useful in the present invention. Examples of suitable hydrophobically modified hydrophilic monomers include, but are not limited to, alkyl acrylates, alkyl methacrylates, alkyl acrylamides, alkyl methacrylamides alkyl dimethylammoniummethyl methacrylate halides, and alkyl dimethylammoniumpropyl methacrylamide halides, wherein the alkyl groups have from about 4 to about 22 carbon atoms. In an exemplary embodiment, the hydrophobically modified hydrophilic monomer comprises octadecyldimethylammoniummethyl methacrylate bromide, hexadecyldimethylammoniummethyl methacrylate bromide, hexadecyldimethylammoniumpropyl methacrylamide bromide, 2-ethylhexyl methacrylate, or hexadecyl methacrylamide.

[0022] The hydrophobically modified water-soluble polymers formed from the above-described polymerization reaction may have estimated molecular weights in the range of from about 100,000 to about 10,000,000 and mole ratios of the hydrophilic monomer(s) to the hydrophobically modified hydrophilic monomer(s) in the range of from about 99.98:0.02 to

about 90:10. Suitable hydrophobically modified water-soluble polymers having molecular weights and mole ratios in the ranges set forth above include, but are not limited to, acrylamide/octadecyldimethylammoniumethyl methacrylate bromide copolymer, dimethylaminoethyl methacrylate/hexadecyldimethylammoniumethyl methacrylate bromide copolymer, dimethylaminoethyl methacrylate/vinyl pyrrolidone/hexadecyldimethylammoniumethyl methacrylate bromide terpolymer and acrylamide/2-acrylamido-2-methyl propane sulfonic acid/2-ethylhexyl methacrylate terpolymer.

[0023] In another embodiment of the present invention, the water-soluble relative permeability modifiers comprise a hydrophilically modified water-soluble polymer. The hydrophilically modified water-soluble polymers used in the present invention typically have a molecular weight in the range of from about 100,000 to about 10,000,000. In an exemplary embodiment, the hydrophilically modified water-soluble polymers comprise a polymer backbone comprising polar heteroatoms. Generally, the polar heteroatoms present within a polymer backbone of the hydrophilically modified water-soluble polymers include, but are not limited to, oxygen, nitrogen, sulfur, or phosphorous.

[0024] In one embodiment of the present invention, the hydrophilically modified water-soluble polymers may be a reaction product of a hydrophilic polymer and a hydrophilic compound that are capable of reacting with each other. Such hydrophilically modified water-soluble polymer may be prereacted before they are placed into the subterranean formation or they may be formed by appropriate reaction *in situ*.

[0025] The hydrophilic polymers suitable for forming the hydrophilically modified water-soluble polymers used in the present invention should be capable of reacting with hydrophilic compounds. In certain exemplary embodiments, suitable hydrophilic polymers include, homo-, co-, or terpolymers such as, but not limited to, polyvinylamines, poly(vinylamines/vinyl alcohols), and alkyl acrylate polymers in general. Additional examples of alkyl acrylate polymers include, but are not limited to, polydimethylaminoethyl methacrylate, polydimethylaminopropyl methacrylamide, poly(acrylamide/dimethylaminoethyl methacrylate), poly(methacrylic acid/dimethylaminoethyl methacrylate), poly(2-acrylamido-2-methyl propane sulfonic acid/dimethylaminoethyl methacrylate), poly(acrylamide/dimethylaminopropyl methacrylamide), poly (acrylic acid/dimethylaminopropyl methacrylamide), and poly(methacrylic acid/dimethylaminopropyl methacrylamide). In certain embodiments, the



hydrophilic polymer contains reactive amino groups in the polymer backbone or as pendant groups, which are capable of reacting with hydrophilic compounds. In an exemplary embodiment, the hydrophilic polymers comprise dialkyl amino pendant groups. In an exemplary embodiment, the hydrophilic polymers comprise a dimethyl amino pendant group and at least one monomer comprising dimethylaminoethyl methacrylate or dimethylaminopropyl methacrylamide.

[0026] In other exemplary embodiments of the present invention, the hydrophilic polymers comprise a polymer backbone comprising polar heteroatoms, wherein the polar heteroatoms present within a polymer backbone of the hydrophilic polymers include, but are not limited to, oxygen, nitrogen, sulfur, or phosphorous. Suitable hydrophilic polymers comprising polar heteroatoms within a polymer backbone include homo-, co-, or terpolymers such as, but not limited to, celluloses, chitosans, polyamides, polyetheramines, polyethyleneimines, polyhydroxyetheramines, polylysines, polysulfones, and starches. In an exemplary embodiment, the starch is a cationic starch. A suitable cationic starch may be formed by reacting a starch, such as corn, maize, waxy maize, potato, tapioca, and the like, with the reaction product of epichlorohydrin and trialkylamine.

[0027] The hydrophilic compounds suitable for reaction with the hydrophilic polymers include polyethers comprising halogen; sulfonates; sulfates; and organic acid derivatives. Examples of suitable polyethers include, but are not limited to, polyethylene oxides, polypropylene oxides, polybutylene oxides, and mixtures thereof. Examples of suitable organic acid derivatives include, but are not limited to, octenyl succinic acid; dodecenyl succinic acid; and anhydrides, esters, and amides of octenyl succinic acid or dodecenyl succinic acid. In an exemplary embodiment, the polyether comprises an epichlorohydrin terminated polyethylene oxide methyl ether.

[0028] The hydrophilically modified water-soluble polymers formed from the reaction of a hydrophilic polymer with a hydrophilic compound may have estimated molecular weights in the range of from about 100,000 to about 10,000,000 and may have weight ratios of the hydrophilic polymers to the polyethers in the range of from about 1:1 to about 10:1. Suitable hydrophilically modified water-soluble polymers having molecular weights and weight ratios in the ranges set forth above include, but are not limited to, the reaction product of polydimethylaminoethyl methacrylate with epichlorohydrin terminated polyethyleneoxide

methyl ether; the reaction product of polydimethylaminopropyl methacrylamide with epichlorohydrin terminated polyethyleneoxide methyl ether; and the reaction product of poly(acrylamide/dimethylaminopropyl methacrylamide) with epichlorohydrin terminated polyethyleneoxide methyl ether. In an exemplary embodiment, the hydrophilically modified water-soluble polymers comprise the reaction product of a polydimethylaminoethyl methacrylate with epichlorohydrin terminated polyethyleneoxide methyl ether having a weight ratio of polydimethylaminoethyl methacrylate to epichlorohydrin terminated polyethyleneoxide methyl ether of 3:1.

[0029] In another embodiment of the present invention, the water-soluble relative permeability modifiers comprise a water-soluble polymer without hydrophobic or hydrophilic modification. Examples of suitable water-soluble polymers include, but are not limited to, homo-, co-, and terpolymers of acrylamide, 2-acrylamido-2-methyl propane sulfonic acid, N,N-dimethylacrylamide, vinyl pyrrolidone, dimethylaminoethyl methacrylate, acrylic acid, dimethylaminopropylmethacrylamide, vinyl amine, vinyl acetate, trimethylammoniummethyl methacrylate chloride, methacrylamide, hydroxyethyl acrylate, vinyl sulfonic acid, vinyl phosphonic acid, methacrylic acid, vinyl caprolactam, N-vinylformamide, N,N-diallylacetamide, dimethyldiallyl ammonium halide, itaconic acid, styrene sulfonic acid, methacrylamidoethyltrimethyl ammonium halide, quaternary salt derivatives of acrylamide and quaternary salt derivatives of acrylic acid.

[0030] Among other things, the water-soluble relative permeability modifiers of the present invention when placed into a subterranean zone may provide improved efficiency of injection operations by the diversion of aqueous injection fluids. It is believed that the water-soluble relative permeability modifier, among other things, may attach to surfaces within the subterranean formation. The presence of the water-soluble relative permeability modifier in the subterranean formation may reduce the permeability of the treated zones to aqueous-based fluids without substantially changing its permeability to hydrocarbons. By this modification of the permeability of the treated zones, it is believed that the water-soluble relative permeability modifier may, *inter alia*, divert aqueous injection fluids injected into the formation during subsequent injection operations to other zones of the formation, *e.g.*, from high permeability zones of the formation to less permeable zones.

[0031] In certain embodiments of the present invention, the water-soluble relative permeability modifiers are provided as part of a permeability-modifying injection fluid. The permeability-modifying injection fluids of the present invention generally comprise an aqueous injection fluid and a water-soluble relative permeability modifier.

[0032] The aqueous injection fluid used in permeability-modifying injection fluids of the present invention may be any aqueous-based fluid that is suitable for use in injection operations that does not adversely react with the water-soluble relative permeability modifiers of the present invention. The aqueous injection fluid generally comprises an aqueous-based fluid and additional additives. The aqueous-based fluid may comprise fresh water, salt water (*e.g.*, water containing one or more salts, such as potassium chloride, dissolved therein), brine (*e.g.*, saturated salt water), produced water, or seawater. The additional additives present in the aqueous injection fluid may include any of a wide variety of additives that are typically used in injection operations that do not adversely react with the hydrophobically modified water-soluble polymers of the present invention.

[0033] Sufficient concentrations of the water-soluble relative permeability modifier should be present in the permeability-modifying injection fluids of the present invention to provide the desired level of diversion of aqueous injection fluids. In an exemplary embodiment, the water-soluble relative permeability modifier should be present in the permeability-modifying injection fluids of the present invention in an amount in the range of from about 0.02% to about 10% by weight of the permeability-modifying injection fluid. In an exemplary embodiment, the water-soluble relative permeability modifier should be present in the permeability-modifying injection fluids of the present invention in an amount in the range of from about 0.05% to about 1.0% by weight of the permeability-modifying injection fluid. In an exemplary embodiment of the present invention, the water-soluble relative permeability modifier may be provided in a concentrated aqueous solution prior to its combination with the aqueous injection fluid to form the permeability-modifying injection fluid.

[0034] The permeability-modifying injection fluids of the present invention may be prepared by any suitable method. In an exemplary embodiment, the water-soluble relative permeability modifiers may be metered into an existing injection stream comprising an aqueous injection fluid to form the permeability-modifying injection fluids of the present invention that is injected into the subterranean formation. Among other things, this may allow treatment of the

subterranean formation with the water-soluble relative permeability modifiers without substantial interruption of an ongoing injection operation.

[0035] Sufficient volumes of the permeability-modifying injection fluids may be injected into the subterranean formation via an injection well penetrating the formation to achieve the desired level of diversion of aqueous injection fluids. The permeability-modifying injection fluids may flow through the areas of least resistance, *e.g.*, the high permeability zones, thereby bypassing less permeable zones. It is believed that the water-soluble relative permeability modifier present in the permeability-modifying injection fluids, among other things, may attach to surfaces within the formation and reduce the permeability of the treated zones to aqueous-based fluids. Generally, after the desired volume of the permeability-modifying injection fluid is injected, the injection operation may proceed with injection of only aqueous injection fluids. The volume of the permeability-modifying injection fluids to inject into the formation will be based, *inter alia*, on several properties of the zone to be treated, such as depth and volume of the zone, as well as the permeability and other physical properties of the material in the zone. One of ordinary skill in the art, with the benefit of this disclosure, will be able to determine the desired volume of the permeability-modifying injection fluid to inject for a chosen application.

[0036] In an exemplary embodiment of the present invention, an oxidizer may be injected into the formation after the permeability-modifying injection fluid to restore the formation's original permeability. Among other things, the oxidizer may remove the water-soluble relative permeability modifier from surfaces within the formation where the water-soluble relative permeability modifier may have penetrated undesirable zones.

[0037] In another embodiment of the present invention, the water-soluble relative permeability modifier may be provided in a treatment fluid comprising an aqueous-based fluid and the water-soluble relative permeability modifier. Additional additives suitable for use in subterranean treatment fluids may be added to the treatment fluids of the present invention as desired.

[0038] The aqueous-based fluid used in the treatment fluids of the present invention can be fresh water, salt water (*e.g.*, water containing one or more salts, such as potassium chloride, dissolved therein), brine (*e.g.*, saturated salt water), produced water, or seawater. Generally, the aqueous-based fluid may be any aqueous liquid provided that it does not adversely react with the other components of the treatment fluids.

[0039] Sufficient concentrations of the water-soluble relative permeability modifier should be present in the treatment fluids of the present invention to provide the desired level of diversion of aqueous injection fluids. In an exemplary embodiment, the water-soluble relative permeability modifier generally should be present in the treatment fluids of the present invention in an amount in the range of from about 0.02% to about 10% by weight of the treatment fluid. In an exemplary embodiment, the water-soluble relative permeability modifier should be present in the treatment fluids of the present invention in an amount in the range of from about 0.05% to about 1.0% by weight of the treatment fluid.

[0040] Sufficient volumes of the treatment fluids may be injected into the subterranean formation via an injection well penetrating the formation to achieve the desired level of diversion of aqueous injection fluids. Generally, the treatment fluid is mixed in a batch process and injected into the formation after injection of an aqueous injection fluid is ceased. The treatment fluids may flow through the areas of least resistance, *e.g.*, the high permeability zones, thereby bypassing less permeable zones. It is believed that the water-soluble relative permeability modifier present in the treatment fluids, among other things, may attach to surfaces within the formation and reduce the permeability of the treated zones to aqueous-based fluids. Generally, after the desired volume of the treatment fluid is injected into the formation, the injection operation may proceed with injection of the aqueous injection fluids. The volume of the treatment fluids to inject into the formation will be based, *inter alia*, on several properties of the zone to be treated, such as depth and volume of the zone, as well as the permeability and other physical properties of the material in the zone. One of ordinary skill in the art, with the benefit of this disclosure, will be able to determine the desired volume of the treatment fluids to inject for a chosen application.

[0041] Moreover, in an exemplary embodiment, after the treatment fluids of the present invention are injected in the subterranean formation, an after-flush of a hydrocarbon liquid, such as kerosene, diesel oil or crude oil, or a hydrocarbon or inert gas, such as methane and natural gas or nitrogen (when the formation produces gas), optionally may be introduced into the formation.

[0042] In an exemplary embodiment of the present invention, an oxidizer may be injected into the formation after the treatment fluid to restore the formation's original permeability. Among other things, the oxidizer may remove the water-soluble relative

permeability modifier from surfaces within the formation where the water-soluble relative permeability modifier may have penetrated undesirable zones.

[0043] In another embodiment of the present invention, the water-soluble relative permeability modifier present in the treatment fluids of the present invention may be formed by the *in situ* reaction between a hydrophilic polymer and a hydrophobic compound. Where this reaction occurs *in situ*, the treatment fluids of the present invention generally comprise an aqueous-based fluid, a hydrophilic polymer, a hydrophobic compound, a surfactant, and an optional pH-adjusting agent. Additional additives suitable for use in subterranean operations may be added to the treatment fluids of the present invention as desired.

[0044] The aqueous-based fluid used in the treatment fluids in the *in situ* reaction embodiments of the present invention can be fresh water, salt water (*e.g.*, water containing one or more salts, such as potassium chloride, dissolved therein), brine (*e.g.*, saturated salt water), produced water, or seawater. Generally, the aqueous-based fluid may be any aqueous liquid provided that it does not adversely affect the other components of the treatment fluids.

[0045] The hydrophilic polymers used in the *in situ* reaction embodiments may be the same as those described above. The hydrophilic polymers, in the *in situ* reaction embodiments of the present invention, should be present in the treatment fluids in an amount sufficient to provide the desired level of diversion of aqueous injection fluids. In an exemplary embodiment, the hydrophilic polymer is present in the treatment fluids of the present invention in an amount in the range of from about 0.1% to about 10% by weight of the treatment fluid. In an exemplary embodiment, the hydrophilic polymer is present in the treatment fluids of the present invention in an amount in the range of from about 0.2% to about 1.5% by weight of the treatment fluid.

[0046] The hydrophobic compounds used in the *in situ* reaction embodiments may be the same as those described above. The hydrophobic compounds, in the *in situ* reaction embodiments of the present invention, should be present in the treatment fluids in an amount sufficient to provide the desired level of diversion of aqueous injection fluids. In an exemplary embodiment, the hydrophobic compound is present in the treatment fluids of the present invention in an amount in the range of from about 0.01% to about 5% by weight of the treatment fluid. In an exemplary embodiment, the hydrophobic compound is present in the treatment fluids of the present invention in an amount in the range of from about 0.02% to about 0.5% by weight of the treatment fluid.

[0047] In the *in situ* reaction embodiments of the present invention, due to the insolubility of hydrophobic compounds in aqueous fluids, a surfactant may be present in the treatment fluids. The surfactant may be selected, *inter alia*, for its ability to potentially promote the dissolution of the hydrophobic compounds in the treatment fluids of the present invention. The surfactant may be anionic, cationic, amphoteric, or neutral. Thus, surfactants suitable for use in the current invention include, but are not limited to, alkyl ammonium surfactants, betaines, alkyl ether sulfates, alkyl ether sulfonates, and ethoxylated alcohols. Generally, the surfactant is added to the treatment fluids of the present invention in an amount so that the hydrophobic compound disperses in the treatment fluids. In an exemplary embodiment, the surfactant is present in the treatment fluids of the present invention in an amount in the range of from about 0.1% to about 2% by weight of the treatment fluid.

[0048] Optionally in the *in situ* reaction embodiments, the treatment fluids of the present invention, may comprise a pH-adjusting agent. The pH-adjusting agent may facilitate the *in situ* reaction between the hydrophilic polymer and the hydrophobic compound by providing a pH of about 8 or higher in the treatment fluid. Examples of suitable pH-adjusting agents include buffers, alkali metal hydroxides, alkali metal carbonates, alkali metal phosphates, and other similar compounds known by those skilled in the art.

[0049] Depending on certain well bore and formation conditions, a shut-in period of up to about several hours may be required after injection of the treatment fluid to permit the *in situ* reaction between the hydrophilic polymer and the hydrophobic compound. During the shut-in period, the hydrophilic polymer and the hydrophobic polymer react to form the hydrophobically modified water-soluble polymer. Generally, the length of the well bore and the downhole temperature should determine the length of any shut-in period. For example, a deep well bore with temperatures greater than or equal to about 200°F may not require a shut-in period. Moreover, shallower, cooler formations may require longer shut-in periods that may extend up to about 24 hours. Those skilled in the art will be able to readily determine the necessity for, and duration of, any shut-in periods that may be useful to permit the appropriate *in situ* reaction.

[0050] In another embodiment of the present invention, the water-soluble relative permeability modifiers present in the treatment fluids of the present invention may be formed by the *in situ* reaction between a hydrophilic polymer and a hydrophilic compound. Where this reaction occurs *in situ*, the treatment fluids of the present invention generally comprise an

aqueous-based fluid, a hydrophilic polymer, a hydrophilic compound, and an optional pH-adjusting agent. Additional additives suitable for use in subterranean operations may be added to the treatment fluids of the present invention as desired.

[0051] The aqueous-based fluids, hydrophilic polymers, hydrophilic compounds, and pH-adjusting agents suitable for use in these treatment fluids may be the same as those described above.

[0052] The hydrophilic polymers, in the *in situ* reaction embodiments of the present invention, should be present in the treatment fluids in an amount sufficient to provide the desired level of diversion of aqueous injection fluids. In an exemplary embodiment, the hydrophilic polymer is present in the treatment fluids of the present invention in an amount in the range of from about 0.1% to about 10% by weight of the treatment fluid. In an exemplary embodiment, the hydrophilic polymer is present in the treatment fluids of the present invention in an amount in the range of from about 0.2% to about 1.5% by weight of the treatment fluid.

[0053] The hydrophilic compounds, in the *in situ* reaction embodiments of the present invention, should be present in the treatment fluids in an amount sufficient to provide the desired level of diversion of aqueous injection fluids. In an exemplary embodiment, the hydrophilic compound is present in the treatment fluids of the present invention in an amount in the range of from about 0.01% to about 5% by weight of the treatment fluid. In an exemplary embodiment, the hydrophilic compound is present in the treatment fluids of the present invention in an amount in the range of from about 0.02% to about 0.5% by weight of the treatment fluid.

[0054] Depending on certain well bore and formation conditions, a shut-in period of up to about several hours may be required after injection of the treatment fluid to permit the *in situ* reaction between the hydrophilic polymer and the hydrophilic compound. During the shut-in period, the hydrophilic polymer and the hydrophilic compound react to form the hydrophilically modified water-soluble polymer. Generally, the length of the well bore and the downhole temperature should determine the length of any shut-in period. For example, a deep well bore with temperatures greater than or equal to about 200°F may not require a shut-in period. Moreover, shallower, cooler formations may require longer shut-in periods that may extend up to about 24 hours. Those skilled in the art will be able to readily determine the necessity for, and duration of, any shut-in periods that may be useful to permit the appropriate *in situ* reaction.



[0055] An exemplary method of the present invention for performing an injection operation comprises: introducing a water-soluble relative permeability modifier comprising a hydrophobically modified water-soluble polymer into a subterranean formation; and injecting an aqueous injection fluid into the subterranean formation after introducing the water-soluble relative permeability modifier.

[0056] Another exemplary method of the present invention for performing an injection operation comprises: introducing a water-soluble relative permeability modifier comprising a hydrophilically modified water-soluble polymer into a subterranean formation; and injecting an aqueous injection fluid into the subterranean formation after introducing the water-soluble relative permeability modifier.

[0057] Another exemplary method of the present invention for performing an injection operation comprises: providing a water-soluble relative permeability modifier comprising a water-soluble polymer without hydrophobic or hydrophilic modification; introducing the water-soluble relative permeability modifier into a subterranean formation; and injecting an aqueous injection fluid into the subterranean formation after introducing the water-soluble relative permeability modifier.

[0058] An exemplary embodiment of a permeability-modifying treatment fluid of the present invention comprises a water-soluble relative permeability modifier comprising a hydrophobically modified water-soluble polymer.

[0059] Another exemplary embodiment of a permeability-modifying treatment fluid of the present invention comprises a water-soluble relative permeability modifier comprising a hydrophilically modified water-soluble polymer.

[0060] Another exemplary embodiment of a permeability-modifying treatment fluid of the present invention comprises a water-soluble polymer without hydrophilic or hydrophobic modification.

[0061] To facilitate a better understanding of the present invention, the following examples of the preferred embodiments are given. In no way should the following examples be read to limit, or define, the scope of the invention.

### **EXAMPLES**

[0062] A fluid diversion test was performed using a “parallel” core set up. In the parallel set up, a High Permeability core (a Brown Sandstone Core) and a Low Permeability core (a

Berea core) were connected in parallel so that a sample fluid has equal opportunity to enter either core. This test was conducted at 175°F. This test was conducted using a brine containing 9% sodium chloride and 1% calcium chloride by weight.

[0063] The sample fluid used in this test comprised 2000 ppm of a hydrophobically modified water-soluble polymer dissolved in a 2% potassium chloride solution by weight. The hydrophobically modified water-soluble polymer was a dimethylaminoethyl methacrylate/hexadecyldimethylammoniummethyl methacrylate bromide copolymer.

[0064] The following procedure was used for this test, the results of which are provided in Table 1. The High Permeability core was taken to residual oil saturation by flowing a sequence of brine-oil-brine. The Low Permeability core was taken to residual water saturation by flowing a sequence of brine-oil-brine-oil. The cores were then connected in parallel set up, and the sample fluid was pumped into the two cores, wherein 93% of the sample fluid entered the High Permeability core and 7% of the sample fluid entered the Low Permeability core. Next, an overflush of a 5% ammonium chloride solution by weight was pumped into the two cores in the parallel set up, wherein 0% of the ammonium chloride solution entered the High Permeability core and 100% of the ammonium chloride solution entered the Low Permeability core. The results of the test are provided below in Table 1.

**TABLE 1**

	<b>% of Sample Fluid Entering Core</b>	<b>% of Overflush Entering Core</b>
High Permeability core	93%	0%
Low Permeability core	7%	100%

[0065] This example indicates, *inter alia*, that a hydrophobically modified water-soluble polymer used in the permeability-modifying injection fluids (and/or treatment fluids) of the present invention may reduce the permeability of a formation to aqueous-based fluids.

[0066] Therefore, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those which are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims.